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CONTAMINATION OF ATMOSPHERE BY USSR ENTERPRISES WHICH PRODUCE AND REFINE HIGH SULFUR CONTENT PETROLEUM

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The lack of experimental data for the checking of established GOST norms on sanitation protective zones for enterprises producing and refining high sulfur content petroleum, and also the complaints of people living near the Second Baku petroleum enterprise, caused the Institute imeni Erisman to undertake a study of the sources and intensity of contamination of the air by hydrogen sulfide around this enterprise. The oil wells located near one of the towns of Bashkir ASSR and one of the petroleum-refining plants of Povolzh'ye, the crude oil for which contains a large quantity of sulfur and free hydrogen sulfide (up to 0.5 percent) were studied.

The study of the petroleum-refining plant region was made in the fall of 1946 and summer of 1947 and that of the oil fields in the summer of 1947.

The refining plant is located in a flat, sparcely planted region. The living quarters are located to the northeast of the plant about 500 meters from the edge of the grounds and 1,200 meters from the working units. The living quarters are on the leeward side of the plant.

Sources of the escape of gases into the air, hydrogen sulfide in particular, were: (a) reservoirs for stocks of raw materials and intermediate products, (b) combined unit for straight distillation, cracking, reforming, and alkali purification of the cracking distillate, (c) multiple leaks of the system due to corrosion of metals, (d) overflow of petroleum in an underground reservior, (e) drainage of water, and (f) a device for measuring the level of liquid products.

Petroleum with a high sulfur content is very corrosive and causes frequent breaks in the hermetic system. Therefore, the grounds of the plant are systematically contaminated by hydrogen sulfide, which was confirmed by analyses of samples of air taken from the grounds of the plant between the production units. In various samples, the concentration of hydrogen sulfide exceeded the limits allowed in the production units. The data on the distribution of hydrogen sulfide vertically in the air over this plant, obtained by Engineer Gamarnikov of the Institute imeni Erisman, were of great interest. He took samples of air from levels of one to 22 meters on outer platforms of a cracking column. They

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showed that hydrogen sulfide was present on all the levels with a maximum of from one to 7 milligrams per cubic meters at heights of one to 10 meters and only traces at 11 meters or greater.

To make a collection of objective data on the distribution of hydrogen sulfide in the surrounding region, zones of 0.5, 1, 1.5, 2, 2.5, 3 kilometers were set up on the leeward side of the plant.

The samples were taken with the aid of the usual aspirator, and were drawn through two successive compound petrie absorbers, filled with a 2-percent solution of sodium arsenite. The samples were 90-100 liters and were drawn through at the rate of 30 liters per hour, and then the hydrogen sulfide was determined by the Polezhayev method. The samples were taken during the hours of 0800 to 2100. At the test points, observations of meteorological conditions, such as wind direction and velocity, temperature, and humidity, were made at the same time as the samples were taken. During the tests the weather was dry, the temperature was from 20 to 30 degrees centigrade, and the wind velocity was from 4 to 5 meters per second with gusts of 10-12 meters per second.

Hydrogen sulfide was found in 148 of the 179 tests (82.7 percent).

In the zones 0.5, 0.8, and 1.5 kilometers from the plant, 100 percent of tests showed hydrogen sulfide. Some of the tests in the one-kilometer zone did not show hydrogen sulfide but this was probably due to the fact that the entire plant was not operating that day and the wind direction had changed.

In the 2- and 2.5-kilometer zones the percent of positive results was reduced to 76 and 60, respectively.

The average concentration in the zones near the plant (up to the 2-kilometer zone) decreased gradually (for the 0.5-kilometer zone it was 0.35 milligram per cubic meter, and for the 1.5-kilometer zone it was 0.17 milligram per cubic meter) and only in the 2.5- and 3-kilometer zones did it remain at nearly the same level, 0.06 and 0.04 milligram per cubic meter.

The maximum single concentration in the 0.5-, 1.5-, and 2.5-kilometer zones remained fairly constant, around 0.8 milligram per cubic meter, and only at a distance of 3 kilometers did it drop somewhat. But even in this zone, the maximum hydrogen sulfide found was more than half that of the other zones and one twentieth of the limits allowed for the working units.

Thus, the GOST 2-kilometer sanitation protective zone for petroleum enterprises, established by laboratory research of the Institute imeni Erisman, was completely confirmed and, in any case, it could not be reduced.

Data from an inquiry of people living within the radius of 3.5 kilometers of the plant agreed fully with the laboratory research.

The living quarters of the plant are in a zone 1.2 to 1.8 kilometers from the main source of the escape of gases in the fractioning process. Of the approximately 300 people questioned, 276 said they noticed the smell of hydrogen sulfide; 60 percent stated they felt ill upon noticing the smell of hydrogen sulfide, most of them suffering from dizziness, headaches, and nausea.

Besides this by personal investigation by questioning the people living in in the quarters, it was established that with a southwest wind the smell of hydrogen sulfide was very noticeable in the streets and in the quarters, even with the windows closed.

The second object of the study was the distribution in the immediate neighborhood of one of the towns of an oil field, at which was produced a crude oil that contained a great deal of sulfur (up to 3.7 percent) and free hydrogen sulfide (up to 0.5 percent). During the production, transportation, and processing

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of the crude oil, a petroleum gas composed of hydrogen sulfide and hydrocarbons is released into the air.

Not all the oil wells are connected to the gas-collecting system, and therefore part of the wells release the gas directly into the air. There were over 100 of these wells in 1947. They released into the air nearly 7 tons of gas daily. There were also inactive wells in the field which were not hermetically sealed and, as a result, the petroleum gas was released from them in the same way.

Near the oil field studied there were also two petroleum refineries at which the sources of hydrogen sulfide were the reservoirs of crude oil and intermediate products and also individual production units.

Besides these sources, there were some lesser ones, such as pumps for tanks, compressor systems, oil and gas pipe systems, and lines for feeding oil and petroleum products into cisterns. On the grounds of the oil field, there is a lake which has been strongly contaminated by crude oil.

Petroleum gas from the wells is conducted in gas lines under vacuum to a refining plant, where it is treated to remove the hydrogen sulfide at a "Teyloks" unit. The gas then goes into town under $1\frac{1}{2}$-2 atmospheres, pressure, where it is diluted for illumination purposes. The removal of hydrogen sulfide from the gas at the "Teyloks" unit was shown to be inadequate by our tests, which are represented in the following table.

Amount of Hydrogen Sulfide Before and After Purification of Gas (in %)

Date	Before Purification	After Purification	Percent of Purification
1. Aug 47	6.51	2.70	59
2. Aug 47	4.95	2.87	43
3. Aug 47	4.79	2.34	51
4. Aug 47	3.30	1.95	41
5. Aug 47	4.29	3.33	20
6. Aug 47	3.24	1.63	50

From the table it can be seen that the gas for illumination purposes has a hydrogen sulfide content of from 1.6 to 3.33 percent and the percent of removal of hydrogen sulfide varies from 20 to 60 percent with an average of 44 percent. With proper operation, and an increase in capacity, it would be possible to attain a significantly larger percentage of removal of not less than 90 percent.

As a result of the strong corrosive properties of hydrogen sulfide, frequent breaks occur in the hermetically sealed illuminating gas lines, which result in escape of the gas into the air at various points.

In this test, the living quarters were quite close to the oil field and oil refinery. The distance from the wells to the plant living quarters was 200-300 meters. The distance from the center of the city to the wells is nearly one kilometer. The city and the majority of the living quarters are to the north and northeast of the field and the refinery, and the prevailing winds are from the southwest and south so that the living quarters are regularly contaminated by hydrogen sulfide.

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To gather laboratory data on the contamination of the air of the town by hydrogen sulfide, samples of air were taken from 21 points in all the main living quarters and various streets of the town. Of the more than 300 samples taken, 260 showed the presence of hydrogen sulfide.

The meteorological conditions during the time of the tests were as follows: in the initial period the weather was changeable with some precipitation, the temperature was 13 to 22 degreees centigrade, the wind was from the south at velocities of 2 to 6 meters per second with gusts of up to 10 meters per second; in the latter period the weather was mostly sunny with some storms, the temperature was 17 to 26 degrees centigrade, the wind was from the north at 1 to 5 meters per second.

In two of the habitation points, a large percentage of negative tests were found (40 to 47 percent). This was due to the considerable change in the wind direction.

For a few days during the time of the tests, the supply of gas in the city was shut off. This presented an opportunity to check the role of the illuminating gas lines in the contamination of the air. Hydrogen sulfide was found in 43.7 percent of the samples taken at that time, while it was found in the same places in 90 percent of the samples and in greater concentrations when the gas was not turned off. This gives a basis for regarding the city gas system as a substantial source of the air contamination.

A study of the air indoors, at the same time the samples were taken in the streets and yards, confirmed the significance of the gas system in the contamination of the air, since the hydrogen sulfide was found inside in concentrations considerably exceeding the concentrations on the streets.

It was shown by our investigations that contamination of the city air was more pronounced during mists than during clear weather. This increased contamination during mists was observed in 70 percent of all the samples, but during clear weather only 28 percent of the samples taken had the higher concentrations. Furthermore, not a single negative sample was obtained during mists.

An inquiry among the more than 200 people revealed that residents of the city and those in the living quarters of the plant often noticed the smell of the hydrogen sulfide and were ill because of it.

The presence in the region of petroleum production of two petroleum refining plants which release considerable amounts of gas into the air, hampers the determination of the distance the hydrogen sulfide is carried from the oil field, and the determination of the size of the necessary sanitation protective zones. Therefore, we conducted a study in regions of another oil field, the petroleum gas of which contains nearly 12 percent of hydrogen sulfide.

In the vicinity of this field, within a radius of 1.5 kilometers, we took 25 samples and in all of them we found hydrogen sulfide.

The physiological effect of the observed small concentrations of gas, of the order of hundredths or tenths of a milligram per cubic meter, has not been studied up to now and, therefore, the evaluation of the data received on the contamination of the air must be based on other considerations, for example: the unpleasant odor of the hydrogen sulfide 'poisons' the air of the living quarters, deprives the people of comfort necessary from a hygienic standpoint, with the normal ventilation of the residence, results in shallow breathing by everyone, and causes a number of minor ailments.

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Although the air samples in all our studies were taken when there was a noticeable and sometimes strong odor of hydrogen sulfide in the air, the concentrations we found were several times lower than those at which the odor of hydrogen sulfide becomes apparent. This is explained by the fact that our system of relatively long air sampling (2 hours) gives, due to the fluctuation of the winds, a lower average concentration of the gas.

To reduce the contamination of the air by hydrogen sulfide the following measures are recommended:

At oil fields: (1) hermetic sealing of the equipment of active wells regardless of the amount of the escaping gas, and sealing of inactive wells; (2) hermetic sealing of equipment of the reservoirs; (3) improvement of the maintenance of gas lines and gas equipment; (4) maximum removal of hydrogen sulfide from gas which is to be used for illumination purposes; and (5) prohibition of the drainage of petroleum into ponds, lowlands, etc.

At refineries, it will be necessary to: (1) remove the sulfur from the petroleum products at the various stages of the process of refining by means of alkali treatment, stabilization, etc., and (2) hermetically seal the reservoirs and gas lines. etc.

The data of the investigation lead to the conclusion that at plants refining petroleum with a high sulfur content, the zone separating the technological units and reservoir yards from the living quarters, should be, even on the windward side, at a distance of not less than 2,000 meters.

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